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Original Article

Synthesis of NiO/ZnO Nanoparticles using 2 Propanol Solvent and their Applications for Methylene Blue Degradation

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The nanoparticles play a significant role in fabrication process which are used at large scale in various fields e.g., sensors, electronics drug delivery, optics, catalysis and in water purification process. Nanoparticles (NiO/ZnO) were synthesized using solgel technique. In this method, 2-propanol was taken to analyze the particle size. Fourier Transform Infrared Spectroscopy (FT-IR) confirmed the presence of ZnO/NiO. Ultraviolet Visible (UV) data recorded a band gap for ZnO that was 4.1 eV while UV spectrum of methylene blue demonstrated a decrease in concentration of methylene blue while using NiO/ZnO as catalyst.

Keywords: Sol-gel, Nanocomposites, Methylene blue, Photocatalyst

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Author's Contribution
All the authors contributed equally.

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Project details. Nil

Introduction:

The existence of nanoparticles in metal oxides are significant while performing fabrication which leads to exchanging their bulk properties. These nanoparticles are widely used in various fields e.g., sensors, electronics drug delivery, optics, catalysis and in water purification process [1]. These nanoparticles have very diverse properties as insulator, metal and semi-conductor which are used in piezoelectric devices, microelectronic circuits and the gas sensors [2]. Zinc oxide are in extraordinary in nature as these have low cost, highly photosensitive and non-toxic. These are used in solar cells, light emitting diodes, photonic crystals, acoustic wave filters, modulator wave guides, transparent conductors and photo detectors. These nanoparticles are unique due to their properties such as they have a band gap of 3.37ev having energy as 60mev [3-8]. The nanoparticles of nickel oxide act as cathode in superconductors [9], because these are super paramagnetic and ferromagnetic in behavior [10]. NiO has a band gap 3.5 eV which behave like p-type semiconductors and applied in various fields such as battery manufacturing, electro chromic film, and gas sensors [11-15]. NiO has been investigated extensively due to its structure. The electrons of NiO are spread over a large range of energy due to strong coulomb repulsion [11, 16].

ZnO based nanocomposites are interesting for photocatalytic degradation because various advantages including direct band gap, anisotropic growth, high electron mobility and simple controlling of its morphology [17]. Montini and co-authors synthesized NiO/ZnO nanocomposite and investigated photocatalytic properties of nanoparticles [18].The aim of this research is to synthesize NiO/ZnO nanoparticles by using 2 propanol as solvent and the application of these nanoparticles as catalyst for methylene blue dye degradation i.e. a harmful dye.

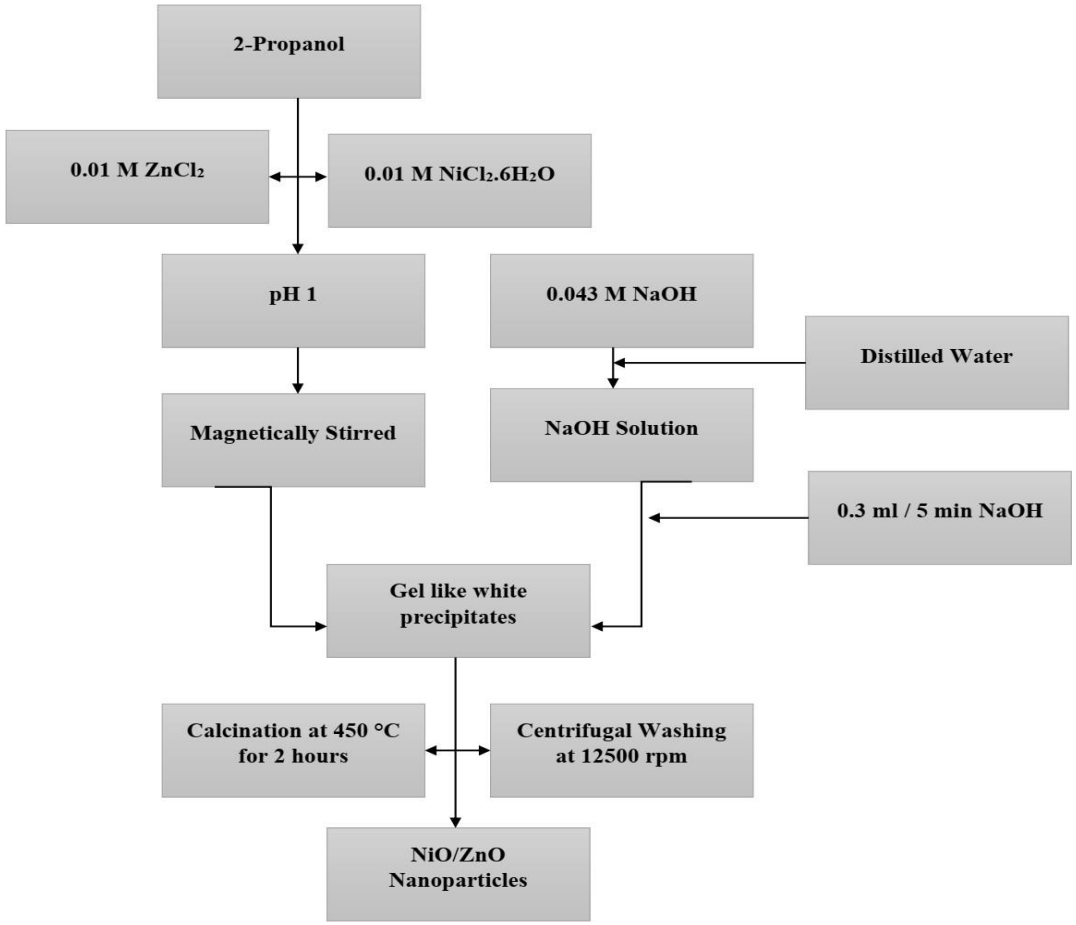

Figure 1 Systematic Synthesis of NiO/ZnO

Material and Methods

NiCl2. 6H2O, Methylene blue and 2-propanol was acquired from sigma Aldrich and ZnCl2 was from Riedl-de-Haen. ZnCl2 was taken 0.013g and NiCl2. 6H2O was taken 0.024g. Both were dissolved in 10 ml 2-propanol. The pH of this solution was measured as 1. The solution was stirred for 5-minutes at room temperature and raised its pH up to 9. Now this solution was centrifuged at 1300rmp for 2-miniutes. To get dry precipitates, we put these in oven overnight and then calcined for two hours at 450°C to obtain oxides only. The chemical reaction is as below:

$NiCl2.6H2O + ZnCl2 + 4NaOH \rightarrow 4NaCl + Ni(OH)2 + Zn(OH)2 + 6H2O$

$Ni^{2+} + Zn^{2+} + 4OH^{-} \rightarrow Ni(OH)2 + Zn(OH)2$

Figure 1 is showing the flow of study adopted in this research to get NiO/ZnO nanoparticles.

NiO and ZnO nanoparticles were investigated for photo catalytic activity. A solution of Methylene blue was prepared in 20ppm and passed through ultraviolet spectrometer. The wavelength of this solution was recorded as 659nm. About 20ml of this solution was taken into a separate beaker and 10mg of NiO/ZnO nanoparticles were added in it. This solution was further passed through ultraviolet spectrometer at a wavelength of 659nm and the catalytic activity of NiO/ZnO was measured.

Results and discussion:

Fourier Transmission Infrared Spectroscopy (FT-IR)

FTIR spectrum of NiO/ZnO nanocomposites was recorded after calcination. Figure 2 is showing the percentage of transmittance at various wavenumbers. The broad absorption band was recorded at a wavenumber of about 3350 cm^{-1} which is attributed to O–H stretching vibrations. The band number at 1631 cm^{-1} is attributed to bending mode (H–O–H). The peak at band number 1416 cm^{-1} is due to symmetric stretching of C=O. A peak was recorded around 880.8417 cm^{-1} which was due to metal oxygen bond while the band number at 637.321 cm^{-1} represents the stretching vibrations of Ni-O-H bond. The peak at band number 470.201 cm^{-1} represents the peak of Ni-O nanoparticles. The absorption band at 470.201 cm^{-1} describes the stretching mode of ZnO which lie between 450 cm^{-1} to 500 cm^{-1} The same results were recorded were reported by various researchers [17,18,19,20,21,22,23].

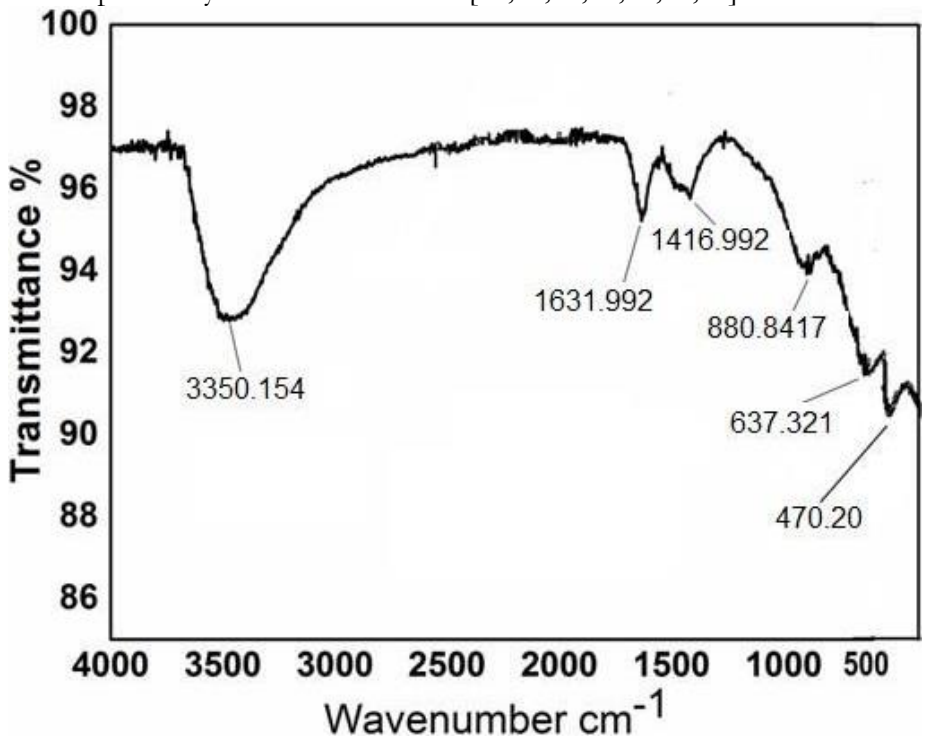

Figure 2 FT-IR of calcined NiO/ZnO

Particle Size Analysis

The particle size of nickel oxide and zinc oxide nanoparticle were measured by taking Bt- 90 analyzer. The results reported that the surface area and the particle size are in inverse relation to each other. Particle size was estimated as 175nm, 139nm, 92nm and 69nm after 1, 2, 3 and 4 hours respectively as showing in Table 1 and Figure 3.

Table 1. Relationship between particle size and the surface area of NiO/ZnO using 2-Propanol as solvent.

Time (hours)	Particle Size (nm)	Specific Area m^2/g
1	175	14.24
2	139	18.22
3	92	22.66
4	69	29.69

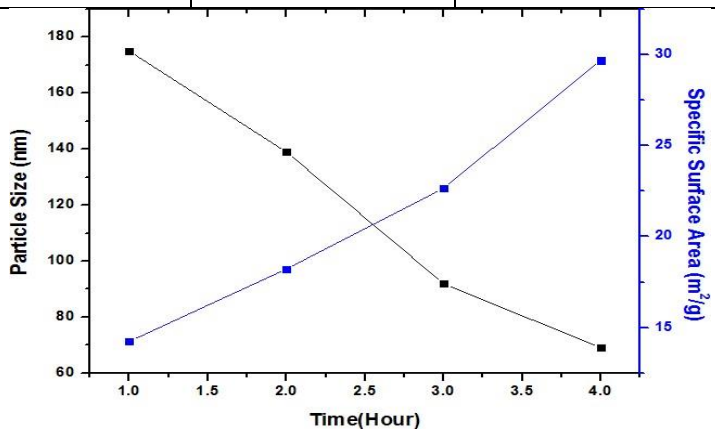

Figure 3 Particle size, time and specific surface area if NiO/ZnO nanoparticles using 2-propanol as solvent

UV- Visible Spectroscopy:

Band gap of NiO and ZnO nanoparticles was measured using the following equation:

$$(h\nu\alpha)^n = A\,(h\nu - E_g) \qquad \text{Eq (1)}$$

In equation (1) "A" indicates the absorption, "Eg" is band gap, "hν" determines the photo energy and "α" represents the absorption coefficient. The value of n is taken as 2 in case of direct transition and ½ for indirect transition.

The band gap of NiO/ZnO was estimated as 4.1ev. Figure 4 is showing the ultraviolet and visible spectrum of NiO/ZnO nanoparticles.

Table 2. Photocatalysis data of methylene blue

Sr. No.	Time (min)	Absorbance
1	Blank	2.986
2	0	2.183
3	15	2.313
4	30	2.298
5	45	2.235
6	60	2.138
7	75	1.620
8	90	1.607
9	105	1.573
10	120	1.324
11	135	1.114
12	150	1.022

13	165	0.853
14	180	0.837
15	195	0.672

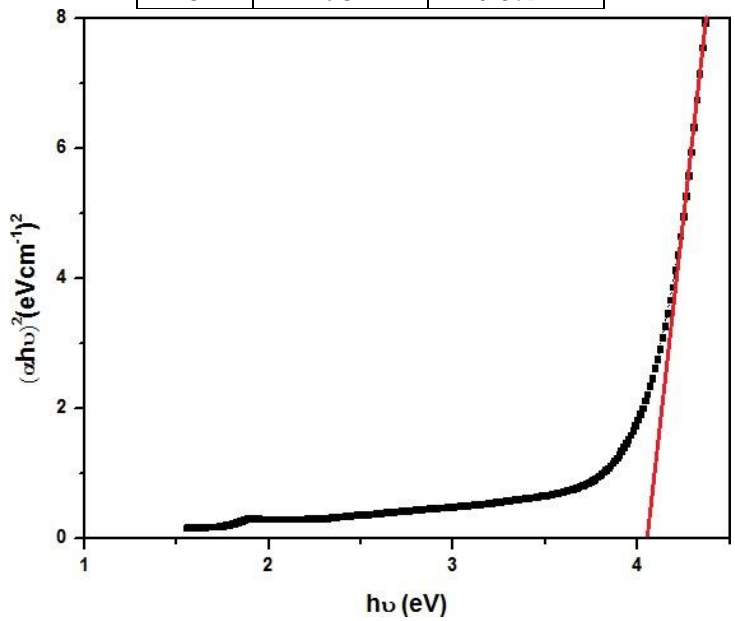

Figure 4: the band gap of NiO/ZnO.

Photocatalytic Activity of NiO/ZnO nanoparticles:

The photocatalytic activity of NiO/ZnO nanoparticles was estimated using UV-visible spectrophotometer with methylene blue. The absorption capacity of the solution was estimated by exposing it to sunlight and the absorption was estimated after every 15 minutes. The absorption capacity was declined with passage of time as shown in Table 2.

Figure 5,6 and 7 are clearly representing the catalytic nature of NiO/ZnO nanoparticles worked. Figure 5 is showing the decrease in absorbance with the passage of time confirming the decreasing concentration of methylene blue in the presence of nanoparticles.

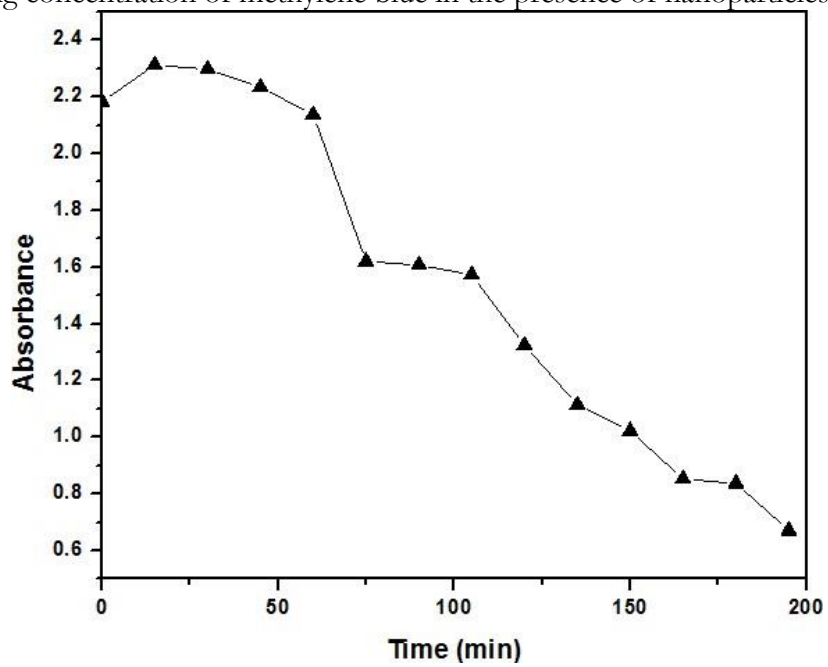

Figure 5 Methylene Blue absorbance with respect to time. Figure 6 is showing that Methylene Blue was degraded with passage of time.

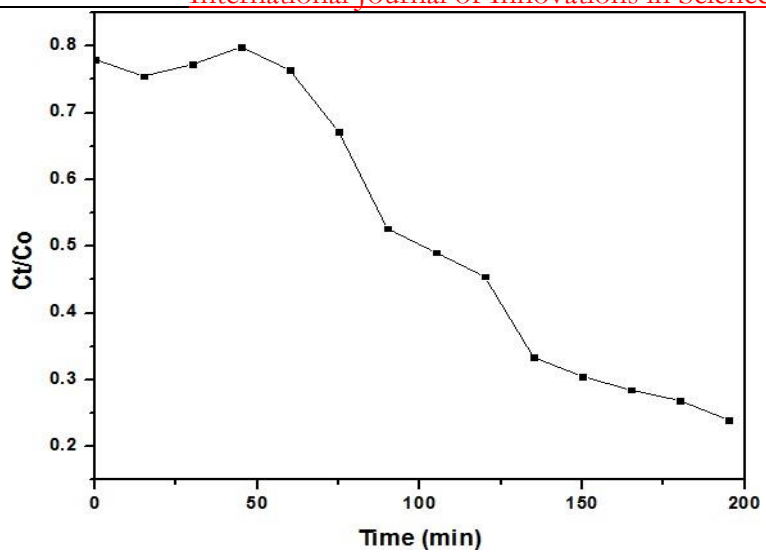

Figure 6 Degradation of MB dye as a function of UV light irradiation time

Figure 7 confirmed that NiO/ZnO nanoparticles degraded the dye up to 75% with passage of time.

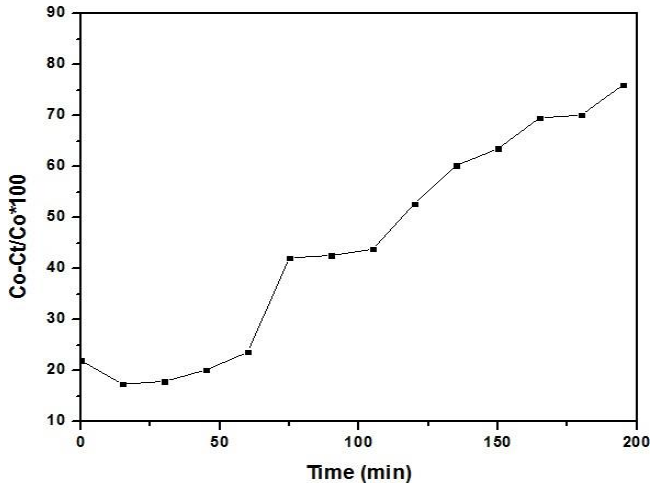

Figure 7 MB degradation efficiency of ZnO NPs

Conclusion:

Nickel oxide and zinc oxide nanoparticles were synthesized using sol-gel method, and the particle size was measured as 69nm and 52.1nm of uncalcined and calcined nanoparticles respectively. A band gap of 4.1ev was measured for NiO and ZnO nanoparticles. Photocatalytic activity of nickel oxide and zinc oxide nanoparticles showed maximum degradation up to 75% under sunlight irradiations. Nickel oxide and zinc oxide nanoparticles can be used as active catalyst for methylene blue degradation.

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